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The Scattering of Electrons by Atomic Systems with Configurations $2p^q$ and $3p^q$

by

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Abstract

The theory is developed describing transitions induced by electron impact between all the ground state terms of atoms and ions with configurations $(2p)^q$ and $(3p)^q$. Full account is taken of exchange and the computed cross sections satisfy exactly the required unitarity bounds. A description is then given of the method used for the solution of the resultant coupled integro differential equations.

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1. Introduction

The interpretation of astronomical observations is helped considerably by a knowledge of the atomic processes which can take place in the constituent elements of astronomical objects. In particular, by studying the observed spectrum one gets some idea of their chemical composition, density and temperature. Many spectral lines observed in gaseous nebulae, in auroras, and in the night airglow are due to transitions, among the terms of atomic systems, which involve no change in the electron configuration of the system. Due to the conservation of parity, these transitions are forbidden for electric dipole radiation but are allowed for electric quadrupole and magnetic dipole radiations. The transition probabilities are of the order (1 to 10^{-5})sec^{-1}, compared with 10^{8} sec^{-1} for permitted dipole lines. The strongest lines in the spectra of most nebulae are due to the $^1D_2$-$^3P_2$ and $^1D_2$-$^3P_1$ magnetic dipole transitions in O^{III}, which has the configuration $(1s)^2\ (2s)^2\ (2p)^2$ in both the initial and final states[1]. Indeed there is considerable astrophysical interest in all the forbidden lines arising from transitions between the three spectral terms of configurations $2p^q$ and $3p^q$, q=2,3,4 in a large number of atoms and ions. These lines can be excited by electron impact. Consequently, it is of interest to predict theoretically the excitation cross sections for electrons incident on atomic systems with configurations $(1s)^2\ (2s)^2\ (2p)^q$ and $(1s)^2\ (2s)^2\ (2p)^6\ (3s)^2\ (3p)^q$.

There is additional astrophysical interest in these transitions for at least two reasons. Firstly, they play an important role in determining the electron density distribution and the electron temperatures in the E and F regions of the upper atmosphere. Secondly, it has been pointed out by Branscomb and Pagel[2] that the absorption of photons by atomic and molecular negative ions, especially C^- and possibly O^-, may be of considerable importance in understanding the physical properties of stellar photospheres. In order to compute the bound-free and free-free absorption coefficients it is necessary to know the radial function describing the motion of the electron, freed by photo-detachment, relative to the parent atom. This is precisely the scattering radial function.

Early calculations of the electron induced transitions in these atoms were shown by Bates et al.[3], to exceed the conservation condition by a large factor. Seaton in a series of papers[4] developed the theory of the continuum Hartree-Fock equations and applied it to a variety of atoms and ions. However, owing to the complexity both of the algebra and of the numerical evaluation of the resulting equations only a few calculations of limited accuracy have been carried out. Recently, the theory has been extended by Seaton and applied by Shemming[5] to calculations of transitions in O^{III}. Both the methods of distorted waves and exact resonance were used in the solution of the resultant coupled integro-differential equations. Recently, also, some exact solutions of a single second order integro-differential equation describing the elastic scattering on the ground state of C [redacted] have been reported by Myerscough and McDowell[6] and on O^+ by Dalgarno, Henry and Stewart [7].

In this paper the theory of scattering of electrons by atomic systems with configurations $2p^q$ and $3q^q$, where q=0 to 6, is developed. Particular emphasis is given to developing the formalism in a way which takes full advantage of the power of high speed digital computers to aid in the algebraic analysis as well in solving the resultant equations. It is found that if a proper treatment of exchange is adopted, then the post-prior discrepancy which troubled early workers in this field does not arise. Further, if only the terms in the ground state configuration of the atom or ion are coupled then the resultant integro-differential equation can be easily solved without further approximation using fast computers. There is very little point in attempting to simplify the equations to use approximate solutions thus introducing further unnecessary errors and ambiguities.

It is convenient to discuss here in general terms the expected accuracy and thus justification of our approach for these transitions. It is by now well known that the close coupling expansion can give results of dubious accuracy for excitation. Thus, in calculating the 1s-2s or 1s-2p excitation by electron impact in atomic hydrogen the 1s-2s-2p close coupling approximation gives results much larger than experiment (Burke and Smith[8]). It is not sufficient to include just a few further

excited states in the expansion but the whole series must be rearranged to obtain faster convergence. However, for elastic scattering on the ground 1s state of hydrogen the approximation obtained by retaining only the 1s state in the expansion gives, when exchange is included correctly, ten per cent accuracy. This is basically because the 1s state is well separated in energy from neighbouring states and is thus weakly coupled. In atoms and ions with configurations $(2p)^q$ and $(3p)^q$ the ground state terms are also well isolated and weakly coupled to other levels. The transitions amongst these terms, is thus more analogous to elastic scattering in hydrogen than to excitation. Thus, provided all the direct and exchange interactions between the terms are included correctly, as in this paper, then the result can be expected to be of fairly high accuracy.

In Sec. (II), the form of the trial function to be substituted into a variational principle is discussed. The use of the principle itself and the derivation of the continuum (i.e. scattering) Hartree-Fock equations is presented in Secs. (III) and (IV). In the final section, (V) we report in detail the numerical methods we have developed to solve the coupled systems of integro-differential equations.

2. The Trial Wave Function

It will be assumed throughout this paper that the Hamiltonian is spin-independent; consequently, both total spin and orbital quantum numbers/are conserved. In order to take advantage of this fact we shall work in a representation which is diagonal in both L and S. It is well known that only approximate solutions can be given to the problems of collision theory; Seaton [4] has shown that the only consistent means of obtaining anti-symmetric wave functions in approximate solutions is to make the expansion explicitly antisymmetric.

S and L respectively,

Consider the collision of an electron with an atomic system with nuclear charge Z and having N electrons, let the totally antisymmetric (N+1) electron wave function be

$$| \Gamma_j : \underline{x}_1 \underline{x}_2 \underline{x}_3 \cdots \underline{x}_{N+1} > \equiv \Psi (\Gamma_j : \underline{X})$$

where $\underline{x}_i$ denotes the spatial and spin coordinates of the ith electron and $\Gamma_j = \gamma_j k_j l_j L_j S_j LSM_L M_S$ is the complete set of quantum numbers required to specify the atomic system in the state j. The atomic term is labelled $L_j S_j$, the wave number and the orbital angular momentum of the projectile are k_j and l_j, respectively. This (N+1) electron wave function can be expanded in terms of basis functions which are completely antisymmetric under interchange of the coordinates of a pair of target electrons

$$| \Gamma_j ; \underline{x}_i \cdots \underline{x}_{N+1} > = \sum_{i=1}^{N+1} (-1)^{N+1-i} (N+1)^{-\frac{1}{2}} \sum_{\Gamma_i} | \Gamma_i : \underline{X}^{-i}, r ; \sigma > F_{ij}(r_i) r_i^{-1} , \qquad \ldots(1)$$

where $\underline{X}^{-i}$ denotes all the coordinates of the (N+1) electrons except those of the ith. and $F_{ij}(r)$ is the function which describes the radial motion of the impinging electron in the channel Γ_i when the system was initially in the state Γ_j. The summation over Γ_i in (1) is restricted in practice to go over the terms belonging to the ground state configuration of the target. It will be shown below that the functions $F_{ij}(r)$ satisfy coupled systems of second order ordinary integro-differential equations with the boundary conditions

$$F_{ij}(r) \underset{r \longrightarrow 0}{\sim} r^{l_i+1}$$

$$\left.\begin{aligned} F_{ij}(r) \underset{r \longrightarrow \infty}{\sim} & \; k_i^{-\frac{1}{2}} (\delta_{ij} \sin\theta_i + \mathcal{R}_{ij} \cos\theta_i) \quad , k_i^2 > 0 \\ \sim & \; e^{-|k_i| r - |\eta_i| \log 2k_i r} \qquad k_i^2 < 0 \end{aligned}\right\} \quad \ldots(2)$$

where $\theta_i = k_i r - l_i \pi/2 - \eta_i \log 2k_i r + \sigma_{l_i}$ $\quad \ldots(3)$

and $\eta_i = -(Z - N) / k_i$.

and $\sigma_{l_i} = \arg \Gamma(l_i + 1 + i\eta_i)$

The radial functions $F_{ij}(r)$ are continuum Hartree-Fock orbitals; from the properties of the surface harmonics $F_{ij}(\underline{r})$ will be automatically orthogonal to atomic discrete orbitals with orbital quantum number $l_\lambda \neq l_i$. For closed subshells, it follows from the antisymmetry of Eq. (1) with respect to the interchange of any two of the electrons that there is no approximation in choosing F_{ij} orthogonal to $P_{n_\lambda l_\lambda}$ even though l_λ might equal l_i. This may be modified slightly if we choose approximate Hartree-Fock orbitals for the target rather than exact H-F orbitals; however, in any case the overlap can be expected to be very small. For incomplete subshells, with $l_\lambda = l_i$ we can expect the overlap integral $(F_{ij}, P) \neq 0$. To take this effect into account, since it is equivalent to the virtual capture of the impinging electron, we have imposed the condition that F_{ij} are orthogonal to <u>all</u> discrete orbitals and added to Eq. (1) an arbitrary amount of a wave function, Ψ_o, corresponding to a configuration with one additional electron in the incomplete subshell. Thus, the trial wave function for the (N+1) electron system in the state Γ_i initially, will be

$$\Psi_t(\Gamma_j; \underline{X}) = |e^- (1s)^2(2s)^2(2p)^q : \Gamma_j : \underline{X}\rangle + C^j \Psi_o [(1s)^2(2s)^2(2p)^{q+1} : LS : \underline{X}] \quad \ldots(4)$$

Equation (4) can be interpreted as a statement of configuration interaction where the first term represents an atomic system with one electron in a continuum orbital, while in the second term all electrons are in discrete orbitals. The coefficients C^j are determined from the variational principle given in the next section. It is assumed that the orbitals $P_{nl}(r)$ do not depend upon the term (e.g. ^3P, ^1D, ^1S for carbon) but only on the configuration and Z. This assumption is vital to our derivation and will be seen to greatly simplify the analysis. The error incurred by this approximation can be expected to be small.

3. Variational Principle

For the asymptotic normalization chosen in Eq.(2), it can be shown, see Burke and Smith[8], that

$$\delta(L - \mathcal{R}/2) = 0 \qquad \ldots(5)$$

provides the basis for a variational principle since the quantity $(L-\mathcal{R}/2)$ is stationary with respect to variations

$$\delta F_{ij}(r) \sim k_i^{-\frac{1}{2}} \delta \mathcal{R}_{ij} \cos\theta_i \qquad \ldots(6)$$

and arbitrary δC^j, where

$$L_{ji} \equiv \int \Psi_t(\Gamma_j; \underline{X})^* (H_{N+1} - E) \Psi_t(\Gamma_i; \underline{X}) \, d\underline{X} \qquad \ldots(7)$$

with the Hamiltonian of the full system being

$$H_{N+1} = \sum_{i=1}^{N+1} (-\tfrac{1}{2} \nabla_i^2 - \frac{Z}{r_i}) + \sum_{i>j=1}^{N+1} \frac{1}{|\underline{r}_i - \underline{r}_j|}. \qquad \ldots(8)$$

We will adopt atomic units with $\hbar = e = m = 1$ throughout.

Upon replacing the first term of Eq.(4) by the expression given in (1) and substituting the result for the first Ψ_t in Eq. (7) we obtain

$$L_{kl} = \int d\underline{X} \left[\sum_{\Gamma_i} (N+1)^{\frac{1}{2}} \Psi_k(\Gamma_i; \underline{X}^{-(N+1)}, \underline{x}_{N+1}) + C^k \Psi_o \right]^*$$

$$\times (H_{N+1} - E) \Psi_t(\Gamma_1; \underline{X}),$$

having used the fact that H_{N+1} is symmetric and Ψ_t is antisymmetric under the interchange of all the coordinates of any pair of electrons. We have introduced the notation

$$\Psi_k(\Gamma_i ; \underline{X}^{-(N+1)}, \underline{x}_{N+1}) = \left| \Gamma_i ; \underline{X}^{-(N+1)}, \hat{r}_{N+1}\, \sigma_{N+1} \right\rangle \frac{F_{ik}(r_{N+1})}{r_{N+1}} \quad \ldots(10)$$

Now substitute the full form for Ψ_t in Eq. (9) and note that the term i=N+1 is distinct from the other N terms to give

$$L_{kl} = \int d\underline{X} \left[\sum_{\Gamma_i} \Psi_k(\Gamma_i; \underline{X}^{-(N+1)}, \underline{x}_{N+1}) + C^k (N+1)^{-\frac{1}{2}} \Psi_o \right]^* (H_{N+1} - E)$$

$$\times \left[\sum_{\Gamma_i} \{ \Psi_l(\Gamma_j; \underline{X}^{-(N+1)}, \underline{x}_{N+1}) - N\, \Psi_l(\Gamma_j; \underline{X}^{-N}, \underline{x}_N) \} + (N+1)^{\frac{1}{2}} C^l \Psi_o \right] \ldots(11)$$

In order to carry out the reduction of the six terms appearing in Eq. (11) we consider separately, the direct term

$$L^D_{ik,jl} = \langle \Psi_k(i, \underline{x}_{N+1}), (H-E)_{N+1}\, \Psi_l(j, \underline{x}_{N+1}) \rangle, \quad \ldots(12)$$

the exchange term

$$L^E_{ik,jl} = -N \langle \Psi_k(i, \underline{x}_{N+1}), (H-E)_{N+1}\, \Psi_l(j; \underline{x}_N) \rangle \quad \ldots(13)$$

terms linear in the arbitrary constants C

$$L^C_{lk} + L^C_{kl} = (N+1)^{\frac{1}{2}} \left[C^l \langle \Psi_o, (H-E)_{N+1} \sum_i \Psi_k(i, \underline{x}_{N+1}) \rangle \right.$$

$$\left. + C^k \langle \Psi_o, (H-E)_{N+1} \sum_i \Psi_l(i, \underline{x}_{N+1}) \rangle \right] \quad \ldots(14)$$

and finally terms quadratic in C

$$L_{kl}^{C^2} = C^k C^l \langle \Psi_o, (H-E)_{N+1} \Psi_o \rangle . \qquad ...(15)$$

To evaluate the matrix element given in Eq. (12), the functions Ψ_k and Ψ_l are replaced by (10) with the composite function of target and spin-angle parts of the projectile wave function being expanded out using Clebsch-Gordan coefficients and Hartree-Fock wave functions for the target which are assumed to satisfy

$$\int \ldots \int d\underline{x}_1 \cdots d\underline{x}_N \; \Psi_{HF}(\underline{x}_1 \ldots \underline{x}_N; L_i S_i) \left[H_N - \delta_{ij} E_N(L_i S_i) \right] \Psi_{HF}(\underline{x}_1 \ldots \underline{x}_N; L_j S_j) = 0 \qquad ...(16)$$

In other words, Ψ_{HF} are so chosen that H_N is diagonal in that representation, where the N electron Hamiltonian is defined in terms of the N+1 Hamiltonian by

$$H_{N+1} = H_N + H_1(\underline{x}_{N+1}) + \sum_{\alpha=1}^{N} r^{-1}_{N+1,\alpha} . \qquad ...(17)$$

where $H_1(\underline{x}_{N+1}) = -\frac{1}{2} \nabla^2_{N+1} - \frac{Z}{r_{N+1}}$.

Using (10), (16) and (17) in (12) we obtain

$$L^{D}_{ik,jl} = \int_0^\infty dr_{N+1} \; F_{ik}(r_{N+1}) \left[-\frac{1}{2} \left(\frac{d^2}{dr^2_{N+1}} - \frac{l_i(l_i+1)}{r^2_{N+1}} + \frac{2Z}{r_{N+1}} + k_i^2 \right) \delta_{ij} \right.$$

$$\left. + V_{ij}(r_{N+1}) \right] F_{jl}(r_{N+1}), \qquad ...(18)$$

where $k_i^2 = 2(E-E_N(L_i S_i))$

is in Rydbergs if E and E_N are in units of 27.2097 eV, and where

$$V_{ij}(r_{N+1}) = \int \Psi^*(\Gamma_i: \underline{X}^{-(N+1)}, \hat{\underline{r}}_{N+1}\sigma_{N+1}) \sum_{a=1}^{N} r_{N+1,a}^{-1} \Psi(\Gamma_j: X^{-(N+1)}, \hat{r}_{N+1} \sigma_{N+1})$$

$$d\underline{x}_1 \ldots d\underline{x}_N \, df_{N+1} \, dr_{N+1}$$

This expression for $V_{ij}(r)$ has been shown by Bely, Tully and Regemorter[9] to reduce to

$$V_{ij}(r) = \delta_{ij} \sum_{\substack{n'l' = \text{closed} \\ \text{subshells}}} 2(2l'+1)\, y_o(P_{n'l'}, P_{n'l'}; r)$$

$$+ \delta_{S_i S_j}\, 3q\, [(2l_i+1)(2L_i+1)(2l_j+1)(2L_j+1)]^{\frac{1}{2}} \sum_{\lambda} (2\lambda+1)^{-1}$$

$$x\, (l_i l_j\, oo \mid \lambda o)\, (1\ 1\ 00 \mid \lambda o)\, W(l_i L_i\, l_j\, L_j;\, L\, \lambda) \sum_{L_2 S_2} (-1)^{L+L_i+L_j+L_2}$$

$$x(q\, L_i S_i \,/\!/\, L_2 S_2)\, (q\, L_j\, S_j \,/\!/ L_2 S_2)\, W(|L_i|L_j; L_2\, \lambda)\, y_\lambda\, (P_{np}\, P_{np}; r), \quad \ldots(19)$$

where n is the principal quantum number of the outermost incomplete p- subshell, (ab oo|co) is a Clebsch-Gordan coefficient, W(abcd; ef) a Racah coefficient, both in the phase convention of Blatt, Biedenharn and Rose[10] and $(q\, L_i S_i \,|\!\}\, L_2\, S_2)$ is the coefficient of fractional parentage.

In the evaluation of the exchange term, Eq. (13), we note that the matrix element $\langle H_N \rangle$ will include and overlap integral

$$\int d\underline{x}_{N+1}\, F_{ik}(\underline{x}_{N+1})\ R_{2p}(\underline{x}_{N+1}) \qquad \ldots(20)$$

which, as discussed in Sec. (II), we are going to set equal to zero. The matrix element of the single electron Hamiltonian, $H_1(\underline{x}_{N+1})$, will contain a similar factor to (20). Consequently, (13) simply becomes

$$L^E_{ik,jl} = -N \int\cdots\int d\underline{x}_1 \cdots d\underline{x}_{N+1}\, \Psi_k(i, \underline{x}_{N+1}) \frac{1}{|\underline{r}_{N+1}-\underline{r}_N|} \Psi_l(j; \underline{x}_N), \quad \ldots(21)$$

since those terms in Σ_α with $\alpha \neq N$ will all have overlap integrals like those of (20). Equation (21) was evaluated using the methods of Hartree[11] and Racah[12] and we obtain

$$L^E_{ik,jl} \equiv \int dr_{N+1}\, F_{ik}\, W_{ij}\, F_{jl}$$

$$= -\delta_{ij} \sum_{\substack{n'l' \\ = \text{closed} \\ \text{subshells}}}{}' \sum_\lambda R_\lambda(P_{n'l'}\, F_{ik}\, F_{jl}\, P_{n'l'})\,(2l'+1)\,(2l_i+1)^{-1}$$

$$\times (l'\,\lambda oo \,|\, l_i o)^2 \; -3q\,[(2l_i+1)(2L_i+1)(2S_i+1)(2l_j+1)(2L_j+1)(2S_j+1)]^{\frac{1}{2}}$$

$$\times \sum_{L_2 S_2} (q\, L_i\, S_i \,\}\, L_2\, S_2)\,(q\, L_j\, S_j \,\}\, L_2\, S_2)\; W(S_j\, \tfrac{1}{2}\, \tfrac{1}{2}\, S_i;\, S S_2)$$

$$\times \sum_\lambda (l_j\, oo \,|\, \lambda o)\,(2\lambda+1)^{-1}\,(l_i o\, o\,|\,\lambda_o) \begin{pmatrix} L_2 & 1 & L_j \\ 1 & \lambda & l_j \\ L_i & l_i & L \end{pmatrix} R_\lambda\,(P_{np}\, F_{ik}\, F_{jl}\, P_{np}), \qquad \ldots(22)$$

where R_λ are the Slater integrals, and $\begin{pmatrix} a & b & e' \\ c & d & e \\ f & f' & g \end{pmatrix}$ is the Wigner 9j coefficient.

In the evaluation of the terms linear in C, both the matrix elements of H_N and E contain overlap factors as in (20) and the second term in (14) becomes

$$L^C_{kl} = (N+1)^{\frac{1}{2}} C^k \sum_i \int d\underline{X} \; \Psi_o(\underline{X}) \left[H_1(\underline{x}_{N+1}) + \frac{N}{r_{N+1,N}} \right] \Psi_1(i, \underline{x}_{N+1})$$

$$= C^k \sum_i \int V_i F_{il} \, dr,$$

where

$$V_i(r) = (N+1)^{\frac{1}{2}} [\delta_{li} \, 1 \, (q+1 \; LS \; | \} \; L_i \; S_i) \left\{ (-\tfrac{1}{2} \frac{d^2}{dr^2} + \frac{1}{r^2} - \frac{Z}{r}) P_{np}(r) \right.$$

$$+ \sum_{\substack{n'l' \\ = \text{closed} \\ \text{subshells}}} 2(2l'+1) \, y_o(P_{n'l'} | P_{n'l'}; r) \, P_{np}(r) + 3q \sum_{L'S'} \delta_{S'S_i} (q+1 \; LS \; | \} \; L'S')$$

$$\times [3(2l_i+1)(2L'+1)(2L_i+1)]^{\frac{1}{2}} \sum_{\lambda L_2 S_2} (-1)^{L_2+L+L'+L_i} (q \; L'S' \; | \} \; L_2 \; S_2)$$

$$\times (q \; L_i S_i \; | \} \; L_2 S_2) \; (2\lambda+1)^{-1} \; (1100 | \lambda \; 0) \; (1l_i \; 00 | \lambda \; 0) \; W(1L' \; l_i \; L_i ; L\lambda)$$

$$\times W(1L' \; 1L_i ; L_2 \; \lambda) \; y_\lambda (P_{np} \; P_{np}; r) \; P_{np}(r) \qquad \ldots(24)$$

It is emphasized that the terms involving C will only appear if electrons are scattered from target systems with incomplete outer p-subshells.

Finally we come to the evaluation of Eq. (15) which does not contain the radial functions F ! Consequently, the matrix element will be simply a number

$$L_{kl} C^2 \equiv C^k C^l (E_{N+1} - E)$$

$$= C^k C^l \left[\sum_{L'S'} (q+1\ LS \,|\}\, L'S')^2 \quad E_N(L'S') - E \right. \qquad \ldots(25)$$

$$\left. + \int dr\ P_{np}(r) \left(-\tfrac{1}{2}\frac{d^2}{dr^2} + \frac{1}{r^2} - \frac{Z}{r}\right) P_{np}(r) + N \langle \Psi_o \,|\, r^{-1}_{N+1,N} \,|\, \Psi_o \rangle \right]$$

where the last matrix element is

$$\sum_{\substack{n'l' \\ = \text{closed} \\ \text{subshells.}}} 2(2l'+1)\, R_o (P_{n'l'}\, P_{np}\, P_{n'l'}\, P_{np}) + q\, \delta_{S'S''} \sum_{L'S'L''} (q+1\ LS \,|\}\, L'S')$$

$$\times (q+1\ LS \,|\}\, L''S') \sum_{\lambda \ell \mathcal{L}} (q\, L'S' \,|\}\, \ell \mathcal{L})\, (qL''\, S' \,|\}\, \ell \mathcal{L})\, q\, [(2L'+1)(2L''+1)]^{\frac{1}{2}}$$

$$\times (1100 \,|\, \lambda 0)^2\, (2\lambda+1)^{-1}\, W(1L'\ 1\ L'';\ L\lambda)\, W(1\ L'\ 1L'';\ \ell\ \lambda)$$

$$\times\ R_\lambda (P^4_{np};\ r)\, (-1)^{L' + L'' + L + \ell} \qquad \ldots(26)$$

Defining D_{ij} by

$$D_{ij} = -\tfrac{1}{2}\left(\frac{d^2}{dr^2} - \frac{l_i(l_i+1)}{r^2} + \frac{2Z}{r} + k_i^2\right) \delta_{ij} + V_{ij} + W_{ij}, \qquad \ldots(27)$$

where W_{ij} is an integral operator given by (22),

Eq. (5) can be written as

$$\delta \left[\sum_{i,j} \int dr\ F_{ik}\, D_{ij}\, F_{jl} + C^k \sum_j \int dr\ V_j\, F_{jl} \right.$$

$$+ C^l \sum_j \int dr\, V_j F_{jk} + C^k C^l (E_{N+1} - E) - \frac{\mu}{2}] = 0, \qquad \ldots(28a)$$

Since we intend to impose the orthogonality of the continuum function to all the discrete orbitals, then extra terms

$$\mu_i \int dr\ P_{np}(r)\ F_{ij}(r)\ \delta_{li^1}, \quad j = k, l \text{ for all } i \qquad \ldots(28b)$$

where μ_i are the Lagrange undetermined multipliers, must be added to Eq. (28a).

4. Radial Equations

Variation of (28) with respect to F_{mn} gives

$$\sum_j \delta F_{mn} D_{mj} F_{jl} \delta_{kn} + \sum_i F_{ik} D_{im} \delta F_{mn} \delta_{ln} + C^k V_m \delta F_{mn} \delta_{ln}$$

$$+ C^l V_m \delta F_{mn} \delta_{kn} + \mu_m P_{np}(r) \delta F_{mn} \delta_{l_m 1} \delta_{kn} + \mu_m P_{np}(r) \delta F_{mn} \delta_{l_m 1} \delta_{ln}$$

$$+ \tfrac{1}{2} \delta \mathcal{R}_{mn} \delta_{mk} \delta_{nl} = 0 \qquad \ldots(29)$$

Using Green's theorem, the second term in (29) can be rewritten and the result is

$$\int dr\, \delta F_{mn}(r) \{ \delta_{kn} [\sum_j D_{mj} F_{jl} + C^l V_m + \mu_m \delta_{l_m 1} P_{np}(r)]$$

$$\ldots(30)$$

$$+ \delta_{ln} [\sum_i D_{mi} F_{ik} + C^k V_m + \mu_m \delta_{l_m 1} P_{np}(r)] \} = 0$$

For arbitrary variations δF, subject to Eq. (6), then

$$\sum_j D_{mj} F_{jl}(r) + C^l V_m + \delta_{l_m 1} \mu_m P_{np}(r) = 0 \qquad \ldots(31)$$

are the system of integro-differential equations for the radial functions F_{jl}^m.

Variation of (28) with respect to C^k yields

$$\delta_{km} \sum_i \int dr\, V_i F_{il} + \delta_{lm} \sum_i \int dr\, V_i F_{ik}$$

$$+ \delta_{km} C^l (E_{N+1} - E) + C^k \delta_{lm} (E_{N+1} - E) = 0, \qquad \ldots(32)$$

which is satisfied by

$$C^{l} = -(E_{N+1} - E)^{-1} \sum_{i} \int dr\, V_i(r)\, F_{il}(r). \qquad \ldots(33)$$

Substituting equation (33) into (31) gives

$$\sum_{j} D_{mj}\, F_{jl}(r) + \frac{1}{E - E_{N+1}}\, V_m(r) \sum_{j} \int dr'\, V_j(r)\, F_{jl}(r') + \delta_{l_m 1}\, \mu_m\, P_{np}(r) = 0 \qquad \ldots(34)$$

These coupled integro-differential equations are solved by the methods described in the next section to yield the radial functions $F_{jl}(r)$. The Lagrangian multiplier's μ_m are adjusted so that the integrals (28b) are zero. The $\mathcal{R}$ matrix can be simply determined from the asymptotic form of the functions $F_{jl}(r)$ according to equation (2a). From the explicit symmetry of the direct and exchange potentials in (34) it follows that the $\mathcal{R}$-matrix is also symmetric and thus the resultant cross section satisfies the required unitarity bounds. The transition matrix T is then defined in the usual way by the matrix relation

$$T = 2i\mathcal{R}/(1 - i\mathcal{R}) \qquad \ldots(35)$$

and the cross section for the transition $L_i\, S_i \longrightarrow L_j\, S_j$ follows immediately from an analysis similar to that given by Lane and Thomas[13]. It is defined by

$$\sigma_{L_i S_i \to L_j S_j} = \sum_{\substack{L\ S\ \pi \\ l_i\ \ l_j}} \frac{(2L+1)(2S+1)}{2k_i^2 (2L_i+1)(2S_i+1)} \left|T_{ij}\right|^2 \qquad \ldots(36)$$

in πa_o^2 units, where L, S, π are the total angular momentum, total spin and parity of the system respectively and where l_i and l_j are the orbital angular momenta of

the initial and final scattered electron states respectively.

In a typical case, for example the scattering of electrons by atomic oxygen, conservation of L S and π implies that (34) reduces to a set of either four of five coupled integro-differential equations for $S=\frac{1}{2}$ depending on whether $L+\pi$ is odd or even respectively.

5. Computer Program to Solve Equations

A FORTRAN program has been written to solve equations (34) for an electron scattered by an atom or ion of arbitrary charge and with the 2p or 3p shell partially filled. The program uses subroutines for the Clebsch-Gordan coefficient $(a\ boo \mid co)$, the Racah coefficient $W(a\ b\ c\ d;\ e\ f)$ and the Wigner 9j coefficient $\begin{pmatrix} a & b & e \\ c & d & e \\ f & f & g \end{pmatrix}$ and a table of relevant fractional parentage coefficients $(q\ L_1\ S_1 \mid\mid L_2\ S_2)$. With this information the program carries out the summations involved in the definitions of $V_{ij}(r)$, W_{ij} and $V_i(r)$ and decides, for a particular L S and π input values, how many equations in (34) are coupled and what the explicit form of all the interaction terms are. It also decides automatically on the basis of the particular atom or ion being considered and the energy of the incident electron, what intervals to use in the numerical integration of (34). The remaining information required by the code in order to carry out the evaluation of the cross section defined by (36) is the Hartree Fock orbitals for the atom or ion. It was found convenient, to read in the analytical orbitals defined by Roothaan and coworkers[14] since they are now available for most of the atoms and ions of interest.

The numerical solution of the resultant coupled equations (34) will now be described. To enable the solution of (34) to be obtained when some or all of the channels are virtual it was necessary to adopt a method of inward and outward integration with subsequent matching to obtain a final continuous solution. This is the method used by Smith and Burke[15]. The integral terms in (34) are treated non-iteratively following Marriott[16] in order that any narrow resonant effects may be determined without convergence difficulties (see Burke and McVicar [17]) Finally the asymptotic expansion method of Burke and Schey [18] was used to determined the $\mathcal{R}$-matrix from the functions F_i. Equation (34) can now be written

$$\frac{d^2 F_i}{dr^2} = \sum_{j=1}^{M} A_{ij}(r)\, F_j(r) + \sum_{k=1}^{NE} a_k\, y_{\lambda_k}(P_k F_k, r)\, P_k(r)$$

$$+ 2CV_i + \delta_{l_i 1}\, \mu_i\, P_{np}(r) \qquad \ldots(37a)$$

where the suffix denoting the incident channel has been dropped since we require all possible solutions of (37) consistent with the boundary conditions (2a). Further the quantity C in (37) is just that given in (33).

According to Hartree[11], the functions $y_\lambda(P\,F;\,r)$ satisfy the following second order ordinary differential equation

$$\frac{d^2}{dr^2}(r\,y_\lambda) = \frac{\lambda\,(\lambda+1)}{r^2}\,(r\,Y_\lambda) - (2\lambda+1)\,\frac{P(r)\,F(r)}{r} \qquad \ldots(37b)$$

with the boundary conditions

$$\begin{aligned} r\,y_\lambda(r) &\underset{r \longrightarrow 0}{\sim} r^{\lambda+1} \\ r\,y_\lambda(r) &\underset{r \longrightarrow \infty}{\sim} r^{-\lambda} \end{aligned} \qquad \ldots(2b)$$

We solve the equation (37) subject to the boundary conditions (2) We now introduce the following definitions: The letter M denotes the number of different F's, i.e. the number of channels; NE is the total number of exchange terms appearing in <u>all</u> the F-equations. Let NA be the number of open channels (i.e. those channels for which $k_i^2 > 0$). We introduce the parameter NV which is zero if all $V_i = 0$, otherwise it is unity. Let NMU be the number of Lagrange multipliers in a given set of equations (37).

At r=0 we define (M+NE) linearly independent solutions of the homogeneous system of equations i.e.

$$Z'' = B.\,Z \qquad \ldots(38)$$

where $Z = \begin{pmatrix} F_i \\ y_k \end{pmatrix}$

is a column vector which has (M+NE) elements. Since Z(0) = 0, then (M+NE) of the arbitrary constants are fixed and the independent solutions are generated by

setting the coefficients of the powers $r^{l_{i+1}}$ or $r^{\lambda+1}$ at the origin unity one at a time with the others set equal to zero. These solutions are then integrated out with $C=\mu_i = 0$. A further (NV + NMU) independent solutions of the inhomogeneous system are generated by setting either C = 1 and all the $\mu_i = 0$, or setting one of the μ_i equal to unity and the remainder, together with C, equal to zero. In this way we define NIN = M + NE + NV + NMU linearly independent solutions at the origin. These solutions are then integrated out to some match point denoted r_o and the NIN solutions are labelled $\mathcal{J}_i^{\alpha}$. These solutions are combined with (as yet unknown) coefficients v_α, where $\alpha=1, \ldots, (M + NE)$, C and μ_i to give the full solution over the range $0 \leq r \leq r_o$. We choose to use the Runge-Kutta method to integrate from r = 0 to a mesh point $h \approx 0.01$ and then the Numerov method from h to r_o.

Asymptotically, where $r = r_B$, (M+NA) linearly independent solutions of Eq. (38) are generated by setting the coefficients of $\sin\theta'$, $\cos\theta'$ and $e^{-\kappa r}$ each in turn to unity, and the remaining coefficients to zero, where $\theta' = kr - \eta \log 2kr$ and $i\kappa=k$. The asymptotic expansion of Burke and Schey is used to calculate the function at r_B and $(r_B - H)$ where H is another stepping increment. These solutions are integrated in to some point r_A, where the exponential terms in the various potentials might be expected to begin contributing. At r_A a further NE linearly independent solution are generated by setting the coefficients of $r^{-\lambda}$ in turn to unity and all others to zero. A further (NV+NMU) independent solutions of the inhomogeneous system are defined by setting C or μ_i equal to unity as in the inner region. The totality of outer solutions, NOUT = N+NA + NE + NV + NMU are integrated from r_A into r_o and beyond to some r_o'. These outer solutions are labelled $\mathcal{G}_i^{\beta}$.

In order that the solution be continuous over the whole domain $0 \leq r \leq r_B$, it is possible to impose continuity of functions and derivatives at any point, e.g. at r_o, or the functions be continuous at a pair of points r_o and r_o' say. The latter criterion was used in the computer program, and gives 2(M+NE) equations

$$\sum_{\alpha=1}^{M+NE} v_\alpha \begin{pmatrix} \mathcal{F}_i^{\alpha}(r_o) \\ \mathcal{F}_i^{\alpha}(r_o') \end{pmatrix} + 2C \begin{pmatrix} \mathcal{F}_i^{C}(r_o) \\ \mathcal{F}_i^{C}(r_o') \end{pmatrix} + \sum_{\gamma=1}^{NMU} \mu_\gamma \begin{pmatrix} \mathcal{F}_i^{\gamma}(r_o) \\ \mathcal{F}_i^{\gamma}(r_o') \end{pmatrix}$$

...(39)

$$= \sum_{\beta=1}^{M+NE+NA} \omega_\beta \begin{pmatrix} \mathcal{G}_i^{\beta}(r_o) \\ \mathcal{G}_i^{\beta}(r_o') \end{pmatrix} + 2C \begin{pmatrix} \mathcal{G}_i^{C}(r_o) \\ \mathcal{G}_i^{C}(r_o') \end{pmatrix} + \sum_{\gamma=1}^{NMU} \mu_\gamma \begin{pmatrix} \mathcal{G}_i^{\gamma}(r_o) \\ \mathcal{G}_i^{\gamma}(r_o') \end{pmatrix} ,$$

for the $2(M+NE) + NA + NV + NMU$ unknown parameters v_α, ω_β, C and μ_γ. A further $(NV + NMU)$ equations are obtained by substituting the continuous solution given by Eq. (39) into (33) and also into the equations obtained by requiring (20) to be zero.

The remaining NA equations are obtained by specifying that the coefficients of the sine part of the R.H.S. of Eq. (39) in the asymptotic region equals $k_i^{-\frac{1}{2}} \delta_{ij}$ for $j = 1$ to NA. That is

$$\sum_\beta \omega_\beta \mathcal{G}_i^{\beta} = \omega_1 \mathcal{G}_i^{1} + \omega_2 \mathcal{G}_i^{2} + \ldots + \omega_{NA} \mathcal{G}_i^{NA} + \ldots + \omega_{NA+i} \mathcal{G}_i^{NA+i} + \ldots .$$

$$= \omega_i \mathcal{G}_i^{i} + \omega_{NA+i} \mathcal{G}_i^{NA+i} \quad \text{since the others do not contribute}$$

$$= \omega_i \sin\theta_i' + \omega_{NA+i} \cos\theta_i' \qquad \ldots(40)$$

where $\theta_i' = k_i r - \eta_i \log 2k_i r$. From Eq. (2a)

$$F_{ij}(r) \sim k_i^{-\frac{1}{2}} [(\sin\theta_i' \cos\phi_i - \cos\theta_i' \sin\phi_i) \delta_{ij}$$

$$+ (\cos\theta_i' \cos\phi_i + \sin\theta_i' \sin\phi_i) \mathcal{R}_{ij}]$$

where $\phi_i = l_i \pi/2 - \sigma_{l_i}$. Combining this result with (40) gives the required NA equations

$$\cos \phi_i \ \omega_i{}^j - \sin \phi_i \ \omega_{NA+i}{}^j = k_i^{-\frac{1}{2}} \ \delta_{ij} \qquad \ldots(41)$$

where the superscript j denotes that the linear equations at the matching point for the parameters $v_1 \ldots \mu$ must be solved NA times, with j characterizing these matched solutions. The elements of the real symmetric reactance matrix are then given by

$$\mathcal{R}_{ij} = k_i^{\frac{1}{2}} [\sin \phi_i \ \omega_i{}^j + \cos \phi_i \ \omega_{NA+i}{}^j]. \qquad \ldots(42)$$

Having obtained the $\mathcal{R}$ matrix it is a simple matter of matrix manipulation to obtain the T-matrix and cross section using equations (35) and (36).

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